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PART II]

SECTION A

[Vol. 23

AUTOMORPHIC COLLINEATIONS OF CONICS

BY HARI DAS BAGCHI

(Retd. Hardinge Professor of Higher Mathematics, Calcutta University)

AND

SHIB SHANKAR SARKAR

(Calcutta University Research Scholar)

ABSTRACT

§1. The object of this note is to examine whether for a given collineation Ω there can exist a conic or conics with respect to which Ω is automorphic, and conversely whether for a given conic there can exist any automorphic collineation. A few corollaries and problems follow. We have not seen such a discussion formally worked out anywhere; but an implied reference to automorphic collineations of a given conic hinted by J. W. Young¹ and Graustein² essentially indicates the set of H.C.'s (harmonic collineations) discussed in this note. An apology is needed for the use of the contraction *w.r.t.* to denote the phrase *with respect to*.

§2. As is wellknown, a plane collineation Ω possesses, in general, three invariant points A, B, C and hence three invariant lines, viz., BC, CA, AB . There are special varieties³ of Ω , for which the number of invariant points or lines may be < 3 or > 3 , or may be infinite. A collineation will be defined as *regular*, if it possesses at least three non-collinear points, which are invariant. Choosing the triangle, formed by these points, as the triangle of reference ABC , Ω is represented by:

$$\rho x' = \lambda x, \rho y' = \mu y, \rho z' = \nu z. \quad (1)$$

Let P, Q be a pair of corresponding points with homogeneous co-ordinates $(x, y, z), (x', y', z')$ determined by the collineation Ω and let ξ, η, ζ denote the cross-ratios⁴ of the pencils $(AC, AB; AQ, AP), (BA, BC; BQ, BP)$ and $(CB, CA; CQ, CP)$. If (X, Y, Z) and (X', Y', Z') are the trilinear co-ordinates of P and Q , then

$$x = pX, y = qY, z = rZ,$$

and similarly for x', y', z' . Hence it easily follows that

$$\left. \begin{aligned} \xi &= \frac{Y'}{Y} \bigg/ \frac{Z'}{Z} = \frac{y'}{y} \bigg/ \frac{z'}{z} = \frac{\mu}{\nu}. \\ \text{Similarly,} \quad \eta &= \frac{\nu}{\lambda}, \quad \zeta = \frac{\lambda}{\mu}. \end{aligned} \right\} \quad (2)$$

To be given an invariant point is equivalent to two conditions between the constants of Ω . Since the general form of Ω involves eight independent constants, given three invariant points, Ω admits of *two* independent parameters, which may be taken as $\lambda: \mu: \nu$ or $\xi: \eta: \zeta$.

When the invariant triangle is assigned, any relation between the values of $\xi: \eta: \zeta$ leads to a special form of collineation and *vice versa*. We now define an *anharmonic collineation* as a regular collineation, for which two of the parameters ξ, η, ζ are equal. In other words, it is a regular collineation, for which one of the roots λ, μ, ν is the geometric mean between the other two. We briefly denote an anharmonic collineation by *A.C.*

When $\eta = \zeta$, so that $\lambda^2 = \mu\nu$, we can write:

$$\rho x' = x, \rho y' = ty, \rho z' = t^{-1}z, \quad (3)$$

which thus generates a one-parameter collineation-group, which may be denoted by $\Sigma_{A,t}$, where A indicates the first vertex of the triangle of reference and t is a parameter. We can similarly write down the *A.C.*'s $\Sigma_{B,t}$ and $\Sigma_{C,t}$. An important case is obtained by taking $t = -1$. The *A.C.* is then called a *harmonic collineation* and will be written *H.C.* Thus $\Sigma_{A,-1}$ is the collineation:

$$\rho x' = -x, \rho y' = y, \rho z' = z. \quad (4)$$

The geometrical significance of an *H.C.* is easily seen. For, in this case, $\eta = \zeta = -1$, *i.e.*, the pencils $(BA, BC; BQ, BP)$ and $(CB, CA; CQ, CP)$ are harmonic. This requires A, P, Q to be collinear, and if this line cuts BC in R , then $(A, R; Q, P) = -1$.

The H.C. (4) is a specialised collineation, for which the vertex A and all points on BC are invariant points. The line BC and any line through A are invariant lines. The triangle, formed by A and any two points on BC , is an invariant triangle. While the general regular collineation involves 8 constants, an A.C. involves 7 constants, while an H.C. involves 4 constants only.

The H.C. can be defined by the following direct geometrical process. Let O be a fixed point and l a fixed line not passing through O . If any point P is taken in the plane, and if OP meets l at R and if Q is the harmonic conjugate of P with respect to O, R , then the correspondence (P, Q) is an H.C. We shall denote this H.C. by the notation $\Pi_{O,l}$. Choosing the triangle of reference, as formed by O and any two points on l , the equation to $\Pi_{O,l}$ takes the form (4).

§3. We shall now discuss the conditions which must be fulfilled in order that a *given* regular collineation Ω ($\neq 1$) may be automorphic with respect to some conic. Taking Ω as given by (1) and taking the conic S , referred to the same triangle of reference as:

$$ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy = 0,$$

S will coincide with its transform, if

$$\lambda^2 = \mu^2 = \nu^2 = \mu\nu = \nu\lambda = \lambda\mu, \quad (5)$$

assuming that none of the coefficients in the equation of the conic is zero. But $\mu\nu = \nu\lambda = \lambda\mu$ means that $\Omega = 1$. Hence, of the coefficients f, g, h , one at least should be zero. Suppose $g = 0, f \neq 0, h \neq 0$. If none of a, b, c be zero, the equation (5) again gives $\lambda = \mu = \nu$, i.e., $\Omega \equiv 1$. But if $a = 0, g = 0, f \neq 0, h \neq 0$, we again get $\Omega \equiv 1$. Hence a necessary condition for Ω to be automorphic to S is that at least two of the coefficients f, g, h should be zero. Suppose $g = 0, h = 0$; then the resulting conic, viz.,

$$ax^2 + by^2 + cz^2 + 2fyz = 0$$

coincides with its transform, if $\lambda^2 = \mu^2 = \nu^2 = \mu\nu$, assuming b and c to be not zero. Hence $\lambda : \mu : \nu = -1 : 1 : 1$, so that Ω is the collineation $\Sigma_{A, -1}$. The result is still true, when only one of the coefficients b and c is zero. If, however, $b = c = 0$, the equation of the conic is

$$ax^2 + 2fyz = 0,$$

which coincides with its transform, when $\lambda^2 = \mu\nu$, i.e., when Ω is an A.C. $\Sigma_{A, 1}$.

A similar discussion holds for the cases: $h = 0, f = 0$ and $f = 0, g = 0$. If f, g, h are all zero, then none of a, b, c can be zero, if S be regarded as non-degenerate. The collineation is automorphic w.r.t. the conic:

$$ax^2 + by^2 + cz^2 = 0,$$

if $\lambda^2 = \mu^2 = \nu^2$. The admissible values, which do not make $\Omega \equiv 1$, are given by: $\lambda : \mu : \nu = -1 : 1 : 1$, or, $1 : -1 : 1$, or, $1 : 1 : -1$. Hence Ω coincides with one or other of the H.C.'s $\Sigma_A, -1$, $\Sigma_B, -1$, $\Sigma_C, -1$.

Summarising, we have the following admissible forms for an automorphic collineation Ω , with the corresponding forms for the conic S :—

(a) $\Omega \equiv \Sigma_A, -1$; $S \equiv ax^2 + by^2 + cz^2 + 2fyz$, including the possibility that b or c may be zero.

(b) $\Omega \equiv \Sigma_A, t-t$; $S \equiv ax^2 + 2fyz$.

(c) $\Omega \equiv \Sigma_A, -1$, or $\Sigma_B, -1$ or $\Sigma_C, -1$; $S \equiv ax^2 + by^2 + cz^2$.

Case (c) being a particular case of (a) when $f = 0$, or similarly of $\Sigma_B, -1$, when $g = 0$, or of $\Sigma_C, -1$, when $h = 0$, it is necessary that the three H.C.'s, mentioned in (c), are *simultaneously* relevant.

THEOREM I. *The necessary and sufficient condition that a regular collineation Ω ($\neq 1$) may be automorphic w.r.t. some conic, is that Ω should be an A.C. or its special variety H.C. In other words, one of the three roots of Ω should be the geometric mean between the other two. When this condition is satisfied, there exist an infinite number of conics, satisfying the requirement.*

§4. We shall now consider the converse problem of finding all collineations, which are automorphic w.r.t. a given non-degenerate conic S . The problem admits of ∞^3 solutions, for the 8 disposable constants of Ω have to satisfy 5 relations only, in order that S may coincide with its transform. All these collineations are, by §3, A.C.'s or H.C.'s.

Considering the form of S in (a) in §3, it is evident that BC is the polar of A w.r.t. S . For the form $S \equiv ax^2 + 2fyz$, AB and AC are tangents at B and C . This leads to the following solution of the present problem. Let P be any point in the plane of S and let l be its polar w.r.t. S . Let Q, R be the points of contact of the tangents to S from P . Then taking PQR as the triangle of reference, the collineation

$$\rho x' = x, \rho y' = ty, \rho z' = t^{-1}z,$$

[N.B.—Results similar to (a) and (b) hold when the vertex A is replaced by B or C .]

where t is an arbitrary parameter, is automorphic w.r.t. S . Since the coordinates of P count as two independent parameters, this process gives the general solution of the problem. In the case where $t = -1$, the A.C. becomes an H.C. and Q, R may be replaced by any two points Q', R' on l .

§5. Let us now examine whether two given conics can possess a common automorphic collineation, i.e., whether there exists a collineation, which transforms each of the two conics into itself. From the construction in §4, it follows that P should have the same polar w.r.t. each of the conics. P is thus a vertex of a common self-conjugate triangle of the two conics. The self-conjugate triangle exists uniquely, if the conics intersect in four distinct points; exists in an infinite number of ways, if the conics have double contact; and does not exist in other cases. In the first case, the H.C. $\Pi_{P,l}$ is the required solution. So if PQR is the common self-conjugate triangle of the two conics S_1, S_2 , each of the H.C.'s $\Pi_{P,QR}, \Pi_{Q,RP}$ and $\Pi_{R,PQ}$ is a common automorphic collineation for S_1, S_2 . If S_1, S_2 have double contact and P is the pole of the common chord, then the A.C. $\Sigma_{P,t}$, where t is a parameter, is a common automorph for the two conics.

THEOREM II. *Two general conics possess three common automorphic collineations, which are H.C.'s, but if the conics have double contact, they possess an infinite number of common automorphs, which are A.C.'s.*

§6. A collineation can be found so as to satisfy 8 independent conditions. The following are a few problems, where apparently 9 conditions are involved:—

(i) *To find a collineation, which keeps a conic S and a pair of points P, Q invariant.*

If O is the pole of PQ w.r.t. S , the H.C. $\Pi_{O,PQ}$ is the required collineation.

(ii) *To find a collineation, which keeps a conic S and a pair of lines l, l' invariant.*

If l and l' intersect at O and if L is the polar of O , the H.C. $\Pi_{O,L}$ is the required collineation.

(iii) *To find a collineation, which keeps a conic S , a point P and a line l invariant.*

If O is the point of intersection of l with the polar of P and if L be the polar of O , the H.C. $\Pi_{O,L}$ is the required collineation.

(iv) *To find a collineation, which keeps a conic S invariant and interchanges two given points P and Q .*

Let the line PQ meet S in P', Q' . Let D, D' be the double points of the involution determined by P, Q and P', Q' . Then if L and L' be the polars of D, D' w.r.t. S , the H.C.'s $\Pi_{D,L}$ and $\Pi_{D',L'}$ are the required collineations.

(v) *To find a collineation, which keeps a conic invariant and interchanges two given lines.*

This is the dual of Problem (iv).

It may be remarked that the *special* meanings, ascribed as above to the conventional phrases *anharmonic collineation (A.C.)* and *harmonic collineation (H.C.)* are precisely the same as those adopted in a former paper of the authors, entitled,

“*The relationship between harmonic and anharmonic collineations in a plane*”. [vide *The American Mathematical Monthly*, Vol. 61 (June–July, 1954)].

REFERENCES

1. Cf., J. W. YOUNG, 1930, *Projective Geometry*, p. 119.
2. Cf., W. C. GRAUSTEIN, 1946, *Introduction to Higher Geometry*, p. 273.
3. Cf., E. S. WOODS, 1922, *Higher Geometry*, Ch. VI, Art 41, pp. 83–86.
4. Cf., W. C. GRAUSTEIN, *loc. cit.*, Ch. X, Art. 1, p. 156.

EFFECT OF ACIDS ON THE RATE OF REACTION OF FORMIC ACID BY CHROMIC ACID—PART I*

BY A. V. MAHAJANI AND A. K. BHATTACHARYA

(Department of Chemistry, University of Saugar, Saugar)

THE order of the reaction between formic acid and chromic acid was determined by Dhar.¹ He showed it to be of the first order with respect to chromic acid. The rate of the reaction is markedly influenced by the presence of sulphuric acid, molybdic acid, manganous chloride and manganous sulphate. The present communication deals with the determination of the influence of acetic acid on the rate of reaction.

EXPERIMENTAL

It has been shown by Dhar (*loc. cit.*) that this reaction is quite free from any disturbing effect and that the Ostwald's isolation method can be followed for determining its order. The authors have followed the same method. All the chemicals used were of the B.D.H. or Merck A. R. quality. It was observed by preliminary experiments that aqueous solutions of chromic acid and acetic acid do not at all react with each other at the concentrations studied. 20 ml. of 9.5 N. aqueous formic acid solution were mixed with a 20 ml. of aqueous acetic acid solution of a definite strength. This mixture and N/3 chromic acid solution (aqueous) were maintained at a constant temperature in an electrically heated and regulated thermostat for an hour. 10 ml. of the chromic acid solution were added to the 40 ml. solution of formic acid and acetic acid. 5 ml. of the reaction mixture were pipetted out at different time intervals and the concentration of unreacted chromic acid in it was determined iodometrically. In a series of experiments only the concentration of acetic acid was changed.

A few of the experimental results and the calculated values of the velocity constants are given in Table I.

The values of K for a set decrease slightly with time. Nevertheless they may be taken as fairly constant and the order of the reaction with respect to chromic acid is thus not affected.

The average values of K for different concentrations of acetic acid and at the temperatures 40°, 50° and 60° are shown in Table II. In taking

* Read at the Annual Meeting on 28th December 1954,

the average values for K in a set only first three or four have been taken in account.

TABLE I

3·8 N Formic acid + 1·28 N Acetic acid + N/15 Chromic acid

<i>t.</i> (sec.)	Volume (ml.)	K (first order) $= \frac{2.303}{t} \log \frac{a}{a-x}$
Temp. 40° C.		
0·02255 N Hypo (<i>a</i> - <i>x</i>)		
00	14·70	
875	13·70	0·00008054
2748	11·80	0·00007993
5773	9·30	0·00007934
6542	8·80	0·00007843
9722	6·95	0·00007465
15345	4·70	0·00007465
Temp. 50° C.		
0·02230 N Hypo		
00	14·75	
786	12·95	0·0001659
1806	10·96	0·0001638
3011	9·02	0·0001630
4808	6·85	0·0001596
6950	5·00	0·0001557
10748	2·90	0·0001518
Temp. 60° C.		
0·02230 N Hypo		
00	14·70	
556	12·20	0·0003351
1043	10·40	0·0003311
1560	8·85	0·0003254
2275	7·05	0·0003229
3443	5·00	0·0003132
5853	2·55	0·0002993

TABLE II

Concentration of Acetic Acid	40°	Temperatures 50°	60°
0.00 N	0.00005575	0.0001142	0.0002238
0.08 N	0.00005669	0.0001176	0.0002325
0.32 N	0.00006320	0.0001214	0.0002436
0.64 N	0.00006705	0.0001369	0.0002788
0.96 N	0.00007262	0.0001484	0.0003016
1.28 N	0.00007993	0.0001642	0.0003308
1.60 N	0.00008814	0.0001760	0.0003508
3.20 N	0.0001309	0.0002830	0.0005860

It is thus evident that the velocity coefficient increases with the increase in the concentration of acetic acid.

The values for temperature coefficient are given in Table III.

TABLE III

Concentration of Acetic Acid	Temp. Coefficient	
	K 50°/K 40°	K 60°/K 50°
0.00 N	2.05	1.95
0.08 N	2.05	1.98
0.32 N	1.92	2.06
0.64 N	2.04	2.03
0.96 N	2.04	2.03
1.28 N	2.06	2.01
1.60 N	1.99	1.98
3.20 N	2.15	2.07

The presence of acetic acid in the reaction mixture does not materially affect the value of the temperature coefficient. These results support the observation that the order of the reaction with respect to chromic acid is not altered by acetic acid.

It was observed by Dhar (*loc. cit.*) that sulphuric acid enhances the rate of this reaction. Snethlage² also made similar observations. The following figures show that the effect of the acetic acid in enhancing the rate of the reaction is much smaller than that of sulphuric acid at equal concentrations:—

Concentration	K (Acetic Acid)	K (Sulphuric Acid)
0.64 N	0.00006705 (at 40° C.)	0.0005487 (at 40° C.)
	0.0001369 (at 50° C.)	0.001124 (at 50° C.)
1.60 N	0.00008814 (at 40° C.)	0.001755 (at 40° C.)
	0.0001760 (at 50° C.)	0.003148 (at 50° C.)

Weistheimer and others³ have suggested a probable mechanism for the chromic acid oxidation of formic acid. According to them the formation of a compound or ion containing quadrivalent and pentavalent chromium is an intermediate step in the reaction. The role of acids in enhancing the rate of this reaction may be the promoting of the formation of such intermediate species or free radicals. Further work in this connection is in progress.

The authors are grateful to the University of Saugar for providing research facilities.

REFERENCES

1. DHAR, N. R., 1917, *J.C.S.*, **111**, 707.
2. SNETHLAGE, H. C. S., 1941, *Rec. Trav. Chim.*, **60**, 877.
3. WEISTHEIMER, F. H., 1949, *Chemical Reviews*, **45**, 419.

EMULSION TYPE DERMATOLOGIC VEHICLES*

BY K. C. VARMA

(*Department of Chemistry, University of Saugar, Sagar*)

(Communicated by Dr. A. K. Bhattacharya)

INTRODUCTION

EFFECTIVE topical medication requires uninterrupted release of the active material to the area being treated. Intelligent formulation of a dermatologic preparation to achieve this objective can only be based on the knowledge of the factors which might accelerate or inhibit the transfer of the anti-infective at the desired rate. Although some study has been devoted to the problem, the number of the chemicals both as anti-bacterials and carriers increases at such a fast pace that controlled investigation on their use lags far behind.

HISTORICAL REVIEW

Early studies on the permeability of the skin are responsible for some of the present concepts of the ointment bases. According to Eller and Wolff¹ such studies have been carried out from time to time since 1804, when Mussey proved that, after application of certain drugs to the unbroken skin, these drugs were found in the urine.

It was around 1930 that several investigators²⁻⁴ working with anti-septic ointments pointed out the inefficiency of the ointments when usual oil or wax base is used. Gershenfeld and Miller⁵ recommended the use of water-miscible vanishing cream formulas as bases for bacterial substances. These, he pointed out, being miscible can be diluted with water and are comparable to the conditions found in practice on the human tissue. Clark,⁶ Gershenfeld and Brillhart⁷ and Burnside and Kuever⁸ in succession pointed out the superiority of the emulsion type bases.

Prout *et al.*⁹ who worked with a base containing silica gel combined with such substances as glycerine, liquid petrolatum and various oils observed that higher percentage of water allows greater diffusion. Foley and Lee¹⁰ also observed that "the presence of water in some bases seemed to increase the diffusion of chemicals into agar, resulting in larger zones of inhibition. The results were not consistent, however, for all the chemicals listed".

* Read at the Annual Session on 28th December 1954.

Therefore they concluded that the nature of the chemical or medicament incorporated in a base has as much or perhaps more to do with the bacteriostatic action of the product than does the composition of the base.

These observations regarding the water-containing bases were perhaps responsible for the great deal of work done on the emulsified ointment base formulation. As early as 1932 Maynard¹¹ called attention to the use of synthetic saponifying agent triethanolamine. Goodman¹² and Mumford¹³ suggested several formulas using triethanolamine. Numerous writers including Gershenfeld and Brillhart,⁷ Li and Kuever,¹⁴ Lesser¹⁵ and Powers *et al.*¹⁶ suggested the use of Cholesterol and its derivatives. Other investigators including Mumford,¹³ Brandrup¹⁷ and Casparis and Meyer¹⁸ mentioned the use of various alcohols for emulsifying purposes. Lesser¹⁵ and Fiero¹⁹ suggested the use of hydrogenated oils.

Medical circles also were recognizing the advantages of the emulsified ointment bases. Fantus²⁰ pointed out that generally "ointments are contraindicated in acute inflammatory conditions of the skin because of their 'heating' quality. This is largely due to the fact that, by inhibiting the evaporation of sweat, they check the cooling effect this would exert, in consequence induce hyperemia of the skin". He further pointed out that the cream ointments are an exception to the above proposition, because "the 'heating' qualities of the fat are antagonized by the water incorporated in them by means of emulsification". Mumford¹³ in discussing the role of emulsifying bases in dermatology observed that the application of ordinary bases like petrolatum, lanolin, or a mixture of these offers a barrier for serous discharges of the skin. He mentioned the superiority of the emulsifying ointments as carriers of both oil-soluble and water-soluble ingredients. Traub²¹ called attention to the fact that the patients do not follow instructions or quickly tire of using ointments because the active ingredients are dissolved or suspended in simple greasy bases. Bamber²² and Landon and Zopf²³ also agreed with Fantus²⁰ and Mumford¹³ that the ointments applied to the skin should not interfere with its normal function of radiation of heat and secretion. Sorg and Jones²⁴ also mentioned some of the same undesirable properties.

The following conclusions may be drawn as a result of further review of literature (25 to 57):

1. Diffusion is better from emulsion type dermatologic bases, oil-in-water type being preferred. More extensive study is necessary to prove the claims of some of the newer bases.

2. Properties of the active substance as well as the constituents of the base are important.

3. There is evidence that the drugs have an optimum concentration beyond which the increase in diffusion is not very great.

4. There is some evidence that factors such as solubility and particle size of the medicament, nature of the oil phase and emulsifying agent and pH of the base seem to effect the diffusion.

5. Condition of the skin plays an important role.

However, most of the work done has been in the field of comparison of diffusion from various types of ointment bases. Very little has been done from the point of view of basic factors which might contribute to the diffusion from an emulsion base.

EXPERIMENTAL

A controlled series of *in vitro* experiments were set up in which a number of factors involved in the physical and chemical environment of the medicated emulsions were varied in an orderly fashion and the effects of the variations measured by agar cup-plate procedure.⁵⁸ The purpose was to see if a formulation pattern could be set up that would enable the dermatologist to predict the therapeutic advantages gained or lost by the alteration of certain ingredients. The various factors studied were the nature of the emulsifying agents and their concentration, nature of the oil phase, oil-water ratio, concentration of the anti-infective, pH under experimental conditions, viscosity and the stability of the anti-infectives in various emulsion type vehicles.

The simplest possible emulsion formula was selected. It consisted of the following parts:

Oil	50
Water	50
Emulsifier	q.s.

Antibacterials for incorporation were penicillin G potassium, aureomycin hydrochloride, chloromycetin (chloramphenicol), bacitracin, streptomycin sulfate, Actamer [2, 2'-dithio-bis (4, 6-dichlorophenol)] and Hexachlorophene (2, 2'-dihydroxy-3, 5, 6, 3', 5', 6'-hexachloro diphenylmethane).

The emulsifying agents used in the formula were ammonium stearate, magnesium stearate, triethanolamine, sodium sulforicinate, sodium lauryl

sulfate, Santomerse 3,⁽¹⁾ Aerosol OT,⁽²⁾ Secal,⁽³⁾ Zephiran,⁽⁴⁾ Arlacel 60,⁽⁵⁾ Span 40,⁽⁶⁾ Tween 80,⁽⁷⁾ glyceryl monostearate (self-emulsifying), acacia and bentonite.

The oils incorporated in the different formulas were soybean, olive, sesame, castor, cottonseed, corn, peanut, light liquid petrolatum, and heavy liquid petrolatum.

A typical medicated emulsion prepared from the basic formula was:

Peanut oil	50
Water	50
Tween 80	5
Penicillin	10 units/ml.

In the penicillin series additional emulsions were prepared containing the same oil but emulsified individually with chosen emulsifying agents, and a group was prepared with each of the other selected oils. Other series of emulsions were also prepared in which oil-water ratio was shifted, and the concentration of the emulsifier and the anti-infective varied. The effects of pH under experimental conditions and viscosity were measured and stability of the anti-infective in various emulsion type vehicles was tested. All the emulsions were passed through a hand homogenizer. In general, this formulation pattern was applied to all of the antibacterials included in the study.

CONCLUSIONS

The following conclusions were drawn from the results of the study:

1. The choice of the emulsifying agent is important for a given anti-infective. Nonionic agents are to be preferred for a simple emulsion type dermatologic vehicle, since they form good emulsions and do not possess any activity of their own. An increase in the concentration of nonionic emulsifying agent does not increase the bacteriostatic activity of the anti-infectives.

(1) Dodecylbenzene Sodium Sulfonate: Monsanto Chemical Co., St. Louis, Mo., U.S.A.

(2) Dioctyl Sodium Sulfosuccinate: American Cyanamid Company, New York, N.Y., U.S.A.

(3) Higher fatty acid glycerol ester containing an amine salt: Emulsol Corporation, Chicago, Ill., U.S.A.

(4) Brand of Benzalkonium Chloride: Winthrop Stearns, Inc., New York, N.Y., U.S.A.

(5) Sorbitan Monostearate: Atlas Powder Company, Wilmington, Del., U.S.A.

(6) Sorbitan Monopalmitate: Atlas Powder Company, Wilmington, Del., U.S.A.

(7) Polyoxyethylene Sorbitan Monooleate: Atlas Powder Company, Wilmington, U.S.A.

2. An increase in the concentration of the oil in emulsions prepared with nonionic emulsifiers usually decreases the bacteriostatic activity. This decrease in activity may be due to the sudden increase in viscosity when oil concentration is raised.

3. The antibiotics used generally exhibit better activity in simple emulsions prepared with nonionic emulsifiers, whereas Actamer and Hexachlorophene show better activity in emulsions containing waxes and fatty substances in addition to the nonionic emulsifiers.

4. The antibiotics show good stability in Span 40 and Arlacel 60 emulsions. Chloromycetin, Streptomycin, Actamer and Hexachlorophene are generally stable in all the emulsions in which they show any activity.

5. Chloromycetin, Streptomycin, Actamer and Hexachlorophene show rather definite optimum concentration.

6. The effects of pH variations under experimental conditions were found to be negligible.

7. There is some evidence that the bacteriostatic activity of penicillin, aureomycin, chloromycetin in the emulsions of soybean, olive, sesame, cottonseed, corn, and peanut oils may be governed by the viscosity of the emulsions.

8. There is also some evidence to the effect that the bacteriostatic activity of Actamer and Hexachlorophene may be related to their solubility in the oil phase.

Some more studies are necessary before a definite formulation pattern can be set up to predict the therapeutic effects of the anti-infectives incorporated in certain bases. However, it would be desirable to carry out further studies on simple emulsions since it will be easier for a dermatologist to modify such a formula to suit the needs of the individual patient.

ACKNOWLEDGEMENT

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BIBLIOGRAPHY

1. ELLER, J. J. AND WOLFF, S., 1939, *Arch. Dermatol. and Syphilol.*, **40**, 900.
2. REDDISH, G. F. AND WALES, H. F., 1929, *J. Am. Pharm. Assoc., Sci. Ed.*, **18**, 576.

3. HUSA, W. J. AND RADIN, J. M., 1932, *J. Am. Pharm. Assoc. Sci. Ed.*, **21**, 861.
4. GERSHENFELD, L. AND MILLER, R. E., 1933, *Am. J. Pharm.*, **105**, 186.
5. ———, 1933, *ibid.*, **105**, 193.
6. CLARK, W. C., 1939, *ibid.*, **111**, 228.
7. GERSHENFELD, L. AND BRILLHART, R. E., 1939, *ibid.*, **111**, 430.
8. BURNSIDE, C. B. AND KUEVER, R. A., 1940, *J. Am. Pharm. Assoc., Sci. Ed.*, **20**, 373.
9. PROUT, W. A., EDDLEMAN, M. S. AND HARRIS, R. G., 1940, *ibid.*, **29**, 372.
10. FOLEY, E. AND LEE, C. O., 1942, *ibid.*, **31**, 105.
11. MAYNARD, M. T. R., 1932, *Arch. Dermatol. and Syphilol.*, **25**, 1041;
and 1936, *ibid.*, **34**, 268.
12. GOODMAN, H., 1937, *ibid.*, **36**, 116.
13. MUMFORD, P. B., 1938, *Brit. J. Dermatol. Syphilis.*, **50**, 540.
14. LI, P. L. AND KUEVER, R. A., 1938, *J. Am. Pharm. Assoc., Sci. Ed.*, **27**, 1217.
15. LESSER, M. A., 1939, *Drug. and Cosmetic Ind.*, **44**, 33.
16. POWERS, J. L., LEASK, H. B. AND WARNER, R. S., 1940, *J. Am. Pharm. Assoc., Sci. Ed.*, **29**, 14.
17. BRANDRUP, W., 1937, *Pharm. Ztg.*, **82**, 111.
18. CASPARIS, V. P. AND MEYER, E. W., 1935, *Pharm. Acta Helv.*, **10**, 163.
19. FIERO, G. W., 1940, *J. Am. Pharm. Assoc., Sci. Ed.*, **29**, 187.
20. FANTUS, B., 1936, *J. Am. Med. Assoc.*, **107**, 861.
21. TRAUB, E. F., 1939, *Urol. and Cutaneous Rev.*, **43**, 409.
22. BAMBER, G., 1940, *Brit. J. Dermatol. Syphilis*, **52**, 21.
23. LANDON, F. W. AND ZOPF, L. C., 1943, *J. Am. Pharm. Assoc., Pr. Ed.*, **4**, 251.
24. SORG, N. F. AND JONES, J. W., 1941, *ibid.*, **2**, 400.
25. GIBSON, A. J., PARKER, H. E. AND ALMUS, A., 1941, *ibid.*, *Sci. Ed.*, **30**, 196.
26. FIERO, G. W. AND LOOMIS, T. A., 1942, *ibid.*, *Pr. Ed.*, **3**, 170.
27. BUSSE, L. W., 1943, *ibid.*, **4**, 314.
28. STRAKOSCH, E. A., 1942, *Arch. Dermatol. and Syphilol.*, **46**, 44.
29. ———, 1943, *ibid.*, **47**, 16.
30. ———, 1943, *ibid.*, **47**, 216.
31. ———, 1943, *ibid.*, **48**, 384.

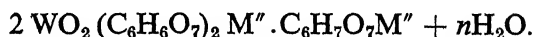
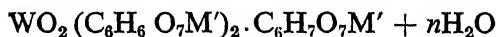
32. STRAKOSCH, E. A. 1944, *Arch. Dermatol. and Syphilol.*, **49**, 1.
33. ———, 1944, *ibid.*, **49**, 8.
34. ALDRICH, D. F. AND DEKAY, H. G., 1945, *J. Am. Pharm. Assoc., Sci. Ed.*, **34**, 17.
35. BANDELIN, F. J. AND KEMP, C. R., 1946, *ibid.*, **35**, 65.
36. HUYCK, C. L., HIROSE, R. S. AND REYES, P. A., 1946, *ibid.*, **35**, 129.
37. GREEN, A. F., 1946, *Quart. J. Pharm. and Pharmacol.*, **19**, 106.
38. CLARK, W. J., 1946, *Am. J. Med. Sci.*, **212**, 523.
39. GOTTSCHALK, H. R., ENGMAN, M. F., MOORE, M. AND WEISS, R. S., 1946, *Arch. Dermatol. and Syphilol.*, **53**, 226.
40. CLYMER, H. A. AND FERLAUTO, R. J., 1947, *J. Am. Pharm. Assoc., Sci. Ed.*, **36**, 211.
41. HART, F. AND HUYCK, C. L., 1947, *ibid.*, **37**, 272.
42. CHRISTENSON, G. L. AND SHELTON, R. S., 1948, *ibid.*, **37**, 354.
43. MEYERS, D. J., NADKARNI, M. V. AND ZOPF, L. C., 1949, *ibid.*, **38**, 231.
44. LOCKIE, L. D. AND SPROWLS, J. B., 1949, *Ibid.*, **38**, 222.
45. LEVY, B. AND HUYCK, C. L., 1949, *Ibid.*, **38**, 611.
46. SKAUEN, D. M., CYR, G. N., CHRISTIAN, J. E. AND LEE, C. O., 1949, *ibid.*, **38**, 618.
47. MILLER, J. L., SLATKIN, M. H. AND JOHNSON, B. A., 1949, *Arch. Dermatol. and Syphilol.*, **60**, 106.
48. CLARK, G. H. AND DAVIES, G. E., 1949, *J. Pharm. and Pharmacol.*, **1**, 521.
49. MILLER, J. L., SLATKIN, M. H., WECHSLER, H. A. AND JOHNSON, B. A., 1950, *Arch. Dermatol. and Syphilol.*, **61**, 648.
50. BARR, M. AND GUTH, E. P., 1951, *J. Am. Pharm. Assoc., Sci. Ed.*, **40**, 13.
51. LOCKIE, L. D. AND SPROWLS, J. B., 1951, *ibid.*, **40**, 72.
52. NADKARNI, M. V., MEYERS, D. B., CARNEY, R. G. AND ZOPF, L. C., 1951, *Arch. Dermatol. and Syphilol.*, **64**, 294.
53. FOSTER, S., WURSTER, D. E., HIGUCHI, T. AND BUSSE, L. W., 1951, *J. Am. Pharm. Assoc., Sci. Ed.*, **40**, 123.
54. BHATIA, V. N. AND ZOPF, L. C., 1952, *ibid.*, **41**, 542.
55. PLEIN, J. B. AND PLEIN, E. M., 1953, *ibid.*, **42**, 79.
56. MACK, W. L., NELSON, J. W. AND GUTH, E. P., 1953, *ibid.*, **42**, 103.
57. WOOD, J. A. AND RISING, L. W., 1953, *ibid.*, **42**, 481.
58. *Compilation of Regulations for the Test and Methods of Assay and Certification of Antibiotics and Antibiotic Containing Drugs*, Vol. 1, Food and Drug Administration, Washington, D. C., U.S.A., 1951.

THE SYSTEMS OF SODIUM TUNGSTATE WITH ORGANIC ACIDS—PART I*

BY G. S. RAO AND S. N. BANERJEE

(Department of Chemistry, University of Saugar, Saugar)

W. PRANDTL AND H. HECHT¹ observed that when a solution of tungstic acid in ammonia is acidified with acetic acid, only a para-tungstate, *i.e.*, a lower tungstate is formed. An oxalato-tungstate having the formula $K_2C_2O_4 \cdot WO_3 + H_2O$ was prepared by Rosenheim² by dissolving WO_3 in potassium oxalate solution. Henderson and Barr³ prepared primary tartrates with tungsten trioxide and showed their composition to be $WO_2 (M'C_4H_4O_6)_2 \cdot nH_2O$. R. Raman and B. L. Vaisya⁴ studied the complex formation between alkali tartrates and tungstate in the alkaline media, and showed that two molecules of tartrate and one molecule of tungstic trioxide are present in the complex. Henderson and co-workers⁵ prepared derivatives of molybdic and tungstic trioxides with citrates, by dissolving one mol. of MoO_3 or WO_3 in two mols. of primary citrates. These workers further observed that molybdenum trioxide forms simple molybdo-citrates while tungsten trioxide forms double salts of tungstic-citrates of the type shown below:



We have studied the systems of sodium tungstate with organic acids, namely, acetic, oxalic, tartaric and citric acids at different concentrations of sodium tungstate, with special reference to the effect of ageing and found that in the case of systems with oxalic, tartaric and citric acids, the results obtained by us are different from those of the previous workers. In this paper we have studied the systems of sodium tungstate with acetic and oxalic acids.

EXPERIMENTAL

For this study, $Na_2WO_4 \cdot 2H_2O$ (A.R.) and chemically pure acetic and oxalic acids have been used. Different sets of sodium tungstate solutions with organic acids were prepared at concentrations of M/32, M/64, and M/128 of sodium tungstate. The conductivity and pH of the systems were measured when fresh and then at intervals of two, four, eight and twelve weeks in order to study the effect of ageing. But the results have been broadly given under

* Read at the Annual Meeting on 28th December 1954.

the classification fresh and aged systems. The experimental details of conductivity and pH measurements are described in a previous communication. The results of conductivity and pH of the fresh and aged system of sodium tungstate with acetic and oxalic acids at concentrations of M/32, M/64 and M/128 of sodium tungstate are given in Tables I to IV and graphed in Figs. 1 and 2.

TABLE I

Conductometric Study of the System Na_2WO_4 -Acetic Acid

Temperature 25° C.

Ratio of Na_2WO_4 to Acetic acid	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	29.65	14.85	14.95	7.55	No change
1:0.5	28.15	29.10	14.80	15.65	8.45	„
1:1.0	28.45	29.55	15.05	16.10	9.55	„
1:1.5	28.50	30.15	16.00	17.50	10.50	„
1:2.0	29.10	31.50	17.15	18.10	11.50	„
1:2.5	30.00	32.50	18.05	19.05	12.55	„
1:3.0	31.35	33.45	20.05	21.05	13.50	„
1:3.5	34.45	36.55	22.35	23.55	15.65	„
1:4.0	39.55	41.65	25.00	26.45	18.50	„
1:4.5	45.10	47.50	27.65	30.05	21.55	„
1:5.0	51.50	51.45	31.50	35.00	25.10	„

TABLE II
Potentiometric Study of Na_2WO_4 -Acetic Acid

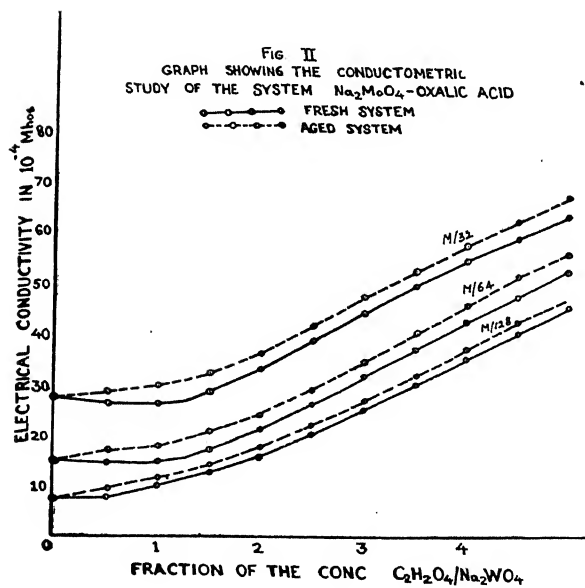
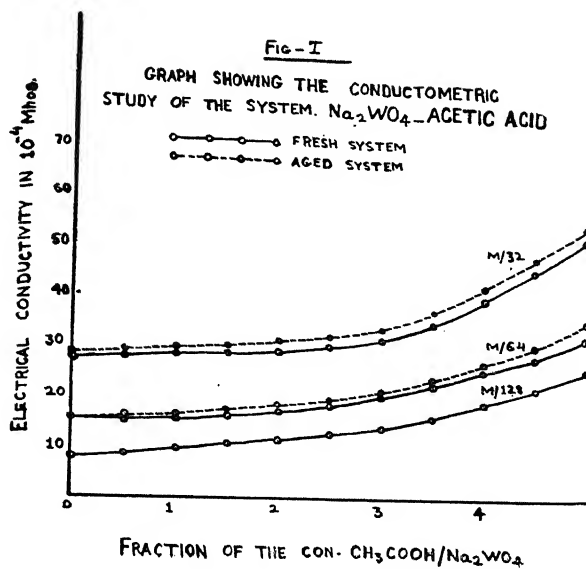
Ratio of Na_2WO_4 to Acetic acid	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.10	6.85	6.80
1:0.5	6.25	6.20	6.40	6.35	6.65	6.60
1:1.0	6.10	6.10	6.05	6.00	6.35	6.30
1:1.5	5.50	5.40	5.55	5.45	6.10	6.05
1:2.0	5.25	5.15	5.25	5.15	5.65	5.55
1:2.5	4.95	4.85	4.95	4.75	5.25	5.20
1:3.0	4.50	4.40	4.85	4.70	5.05	5.00
1:3.5	4.45	4.40	4.75	4.65	4.45	4.85
1:4.0	4.30	4.25	4.55	4.60	4.90	4.80
1:4.5	4.25	4.15	4.65	4.60	4.80	4.65
1:5.0	4.20	4.05	4.30	4.25	4.55	4.45

TABLE III
Conductometric Study of the System Na₂WO₄-Oxalic Acid
Temperature 25° C.

Ratio of Na ₂ WO ₄ to Oxalic acid	Conductivity in 10 ⁻⁴ mhos.					
	Concn. of Na ₂ WO ₄ M/32		Concn. of Na ₂ WO ₄ M/64		Concn. of Na ₂ WO ₄ M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.55	27.65	14.85	14.95	7.55	7.60
1:0.5	26.50	28.50	14.95	17.20	8.05	9.50
1:1.0	26.55	30.05	15.05	18.10	10.50	11.45
1:1.5	28.75	33.10	17.50	20.65	13.10	14.25
1:2.0	33.25	36.50	21.65	23.75	16.10	18.15
1:2.5	39.10	39.50	26.50	29.15	20.50	22.35
1:3.0	44.20	48.10	32.10	35.05	25.50	26.75
1:3.5	50.10	53.10	37.50	41.00	30.45	32.15
1:4.0	55.15	58.50	43.15	46.50	35.65	37.50
1:4.5	59.45	63.10	48.15	52.15	40.85	43.10
1:5.0	54.10	68.10	53.10	56.50	46.10	47.50

TABLE IV
Potentiometric Study of Na₂WO₄-Oxalic Acid

Ratio of Na ₂ WO ₄ to Oxalic acid	pH					
	Concn. of Na ₂ WO ₄ M/32		Concn. of Na ₂ WO ₄ M/64		Concn. of Na ₂ WO ₄ M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.15	6.85	6.75
1:0.5	6.25	5.90	6.30	6.25	6.65	6.60
1:1.0	5.80	5.70	6.05	5.85	6.35	6.25
1:1.5	5.70	5.65	5.85	5.65	6.10	6.05
1:2.0	5.45	5.20	5.65	5.35	5.85	5.80
1:2.5	4.90	4.65	5.35	4.95	5.45	5.35
1:3.0	4.50	4.25	4.95	4.45	5.10	5.05
1:3.5	4.15	3.70	4.60	4.10	4.55	4.50
1:4.0	3.75	3.50	4.15	3.65	3.95	3.85
1:4.5	3.25	2.60	3.65	3.05	3.50	3.35
1:5.0	2.85	2.15	3.10	2.65	2.95	2.90



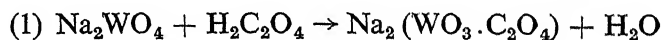
DISCUSSION

The conductivity results of this system (Table I and Fig. 1) show that the conductivity has fallen very slightly with the increase of the ratio of tungstate to acetic acid up to 1 : 3 after which there is a gradual rise in conductivity till the ratio 1 : 5 is reached. The low conductivity of the system upto 1 : 3 and the minimum pH obtained therein show the formation of a lower tungstate, *i.e.*, a para-tungstate as was also observed by Prandtl and Hecht.⁷ On ageing there is considerable increase in conductivity and a slight fall in the pH at all ratios due to hydrolysis of the lower tungstate present.

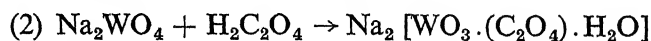
The results of conductivity and pH of the system Na_2WO_4 -Oxalic acid (Tables III and IV, Fig. 1) show inflections at equi-molecular proportions indicating thereby the formation of an oxalato-tungstate complex. The nature of the conductivity and pH results show that the oxalato-tungstate complex has low conductivity and high pH values in comparison with those of components.

The constitution of the oxalato-tungstate can be represented in two ways: (1) as $[\text{WO}_3(\text{C}_2\text{O}_4)]''$ similar to oxalato-molybdate suggested by Ray and Sharma⁸ in which one of the three oxygen atoms occupies two co-ordinate positions, and (2) as an aquo-mono-oxalato-tungstate $[\text{H}_2\text{O} \cdot \text{WO}_3(\text{C}_2\text{O}_4)]''$ similar to aquo-mono-oxalato molybdate, suggested by A. B. Biswas⁹ on the basis of the results of Spittle and Wardlaw¹⁰ and Rosenheim¹¹ in which one molecule of water occupies one of the co-ordinate positions.

The effect of ageing is a significant factor in this system in deciding the constitution of the oxalato-tungstate complex. The formation of the oxalato-tungstate complex can be represented by the following two reactions:



which implies the elimination of a molecule of water and hence the complex formed should be stable even on ageing.



which is additive and does not involve the elimination of water. Hence this complex is less stable and undergoes decomposition on ageing. There is a definite rise in conductivity and fall in pH on ageing, showing thereby, that the complex undergoes decomposition liberating back the components of the complex, *i.e.*, oxalic acid and sodium tungstate. Therefore, the constitution of the oxalato-tungstate complex should be represented as



We express our thanks to Dr. A. K. Bhattacharya for his kind interest in this work.

REFERENCES

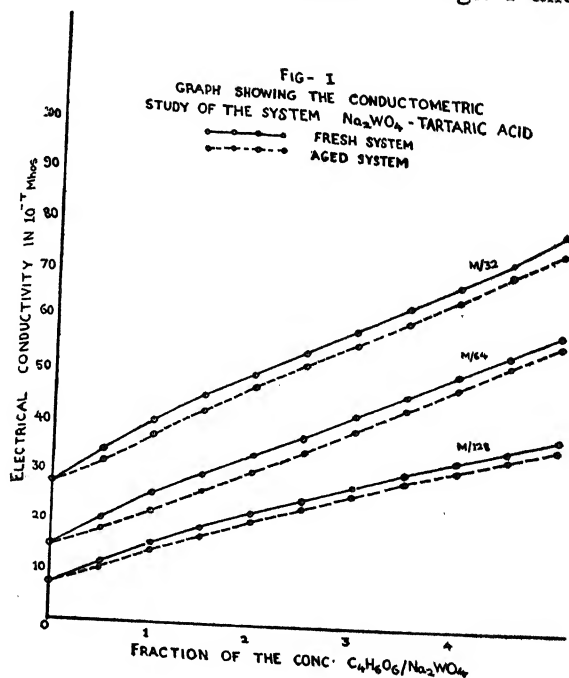
1. PRANDTL, W. AND HECHT, H., 1915, *Ber.*, **48**, 692-698.
2. ROSENHEIM, *ibid.*, **26**, 1191-94.
3. HENDERSON AND BARR, 1899, *J. Chem. Soc.*, 542-58.
4. RAMAN, R. AND VAISHYA, B. L., 1934, *J. Ind. Chem. Soc.*, **11**, 179-84.
5. HENDERSON AND CO-WORKERS, *loc. cit.*
6. RAO AND BANERJI, 1954, *Proc. Nat. Acad. Sci., India*, **23**, 92.
7. PRANDTL AND HECHT, *loc. cit.*
8. RAY, P. AND SHARMA, B., 1944, *J. Ind. Chem. Soc.*, **5**, 149.
9. BISWAS, A. B., 1945, *ibid.*, **12**, 351.
10. SPITTLE AND WARDLAW, 1927, *ibid.*, 1807.
11. ROSENHEIM, 1896, *Z. anorg. Chem.*, **11**, 225.

THE SYSTEMS OF SODIUM TUNGSTATE WITH ORGANIC ACIDS—PART II*

By G. S. RAO

(Department of Chemistry, University of Saugar, Sagar)

In this communication, the systems of sodium tungstate with tartaric and citric acids have been studied. For this study, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ A.R. and chemically pure *d*-tartaric and citric acids have been used. The experimental methods for preparing different sets of solutions of the tungstate and acids to give ratios of tungstate/acid ranging from 1:0 to 1:5 and for the measurement of conductivity and pH are the same as given in Part I of this communication.¹ The conductivity and pH of the systems were measured when fresh and after intervals of two, four, eight and twelve weeks in order to study the effect of ageing. The results are, however, tabulated broadly under the fresh and aged systems. The results of conductivity and pH of the fresh and aged systems of sodium tungstate with tartaric and citric acids at concentrations of M/32, M/64, and M/128 of the tungstate are given in Tables I to IV and represented in Figs. 1 and 2.



* Read at the Annual Meeting on 28th December 1954.

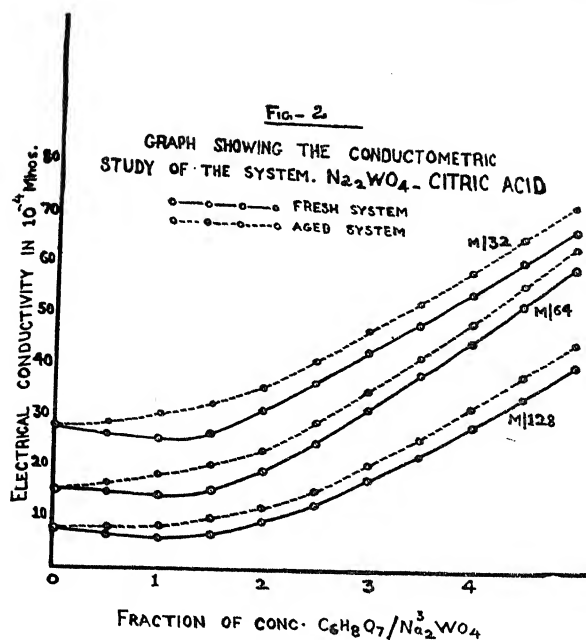


TABLE I
Conductometric Study of Na_2WO_4 - H_2SO_4
Temperature 25°C .

Ratio of Na_2WO_4 to $\frac{1}{2}\text{H}_2\text{SO}_4$	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	27.55	14.85	14.90	7.55	7.60
1:0.5	25.45	25.50	14.10	14.05	7.20	7.25
1:1.0	26.10	28.05	15.15	16.10	8.05	8.50
1:1.5	29.10	30.25	15.85	16.65	8.90	10.05
1:2.0	30.50	31.45	16.45	17.15	9.85	10.50
1:2.5	29.10	31.30	15.65	17.20	9.10	10.50
1:3.0	28.10	31.10	14.70	17.05	8.05	9.50
1:3.5	26.50	28.75	14.10	15.55	6.75	8.75
1:4.0	25.45	26.50	17.20	15.50	10.00	8.10
1:4.5	35.20	31.50	24.15	20.05	15.55	14.50
1:5.0	51.10	40.05	34.00	26.15	21.00	19.35

TABLE II
Potentiometric Study of $\text{Na}_2\text{WO}_4\text{-H}_2\text{SO}_4$

Ratio of Na_2WO_4 to $\frac{1}{2}\text{H}_2\text{SO}_4$	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.05	6.85	6.90
1:0.5	6.35	6.16	6.45	6.30	6.70	6.55
1:1.0	5.55	5.30	5.85	5.70	6.05	6.05
1:1.5	5.10	4.90	5.20	5.10	5.35	5.30
1:2.0	4.55	4.45	4.85	4.75	4.90	4.95
1:2.5	4.30	4.15	4.50	4.45	4.65	4.60
1:3.0	4.20	4.05	4.35	4.20	4.50	4.45
1:3.5	4.15	4.00	4.25	4.00	4.40	4.35
1:4.0	3.60	3.85	3.80	4.00	4.10	4.15
1:4.5	2.45	3.10	3.15	3.35	3.65	3.70
1:5.0	1.55	2.10	2.55	2.45	3.00	3.15

TABLE III
Conductometric Study of the System of $\text{Na}_2\text{WO}_4\text{-H}_3\text{PO}_4$
 Temperature 25° C.

Ratio of Na_2WO_4 to $\frac{1}{3}\text{H}_3\text{PO}_4$	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	27.65	14.85	15.05	7.55	7.60
1:0.5	27.45	28.50	14.90	16.10	7.50	7.65
1:1.0	27.50	28.55	15.05	16.05	7.55	7.60
1:1.5	27.35	28.35	15.00	16.00	7.60	7.70
1:2.0	27.40	28.40	15.10	16.15	7.55	7.75
1:2.5	27.05	28.10	15.05	16.20	7.50	7.65
1:3.0	27.50	29.25	15.55	16.60	7.75	8.10
1:3.5	29.10	31.00	16.45	17.50	8.50	9.05
1:4.0	32.05	33.50	18.10	18.75	9.65	10.05
1:4.5	35.10	36.45	20.65	21.15	10.85	11.15
1:5.0	37.55	39.10	23.20	24.15	14.65	15.55

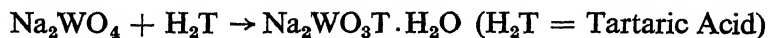
TABLE IV

Potentiometric Study of the System of $\text{Na}_2\text{WO}_4\text{-H}_3\text{PO}_4$

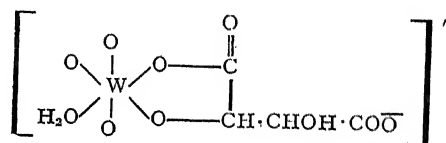
Ratio of Na_2WO_4 to $\frac{1}{3}\text{H}_3\text{PO}_4$	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.05	6.85	6.80
1:0.5	6.15	6.05	6.30	6.15	6.40	6.35
1:1.0	5.60	5.50	5.75	5.65	5.85	5.80
1:1.5	5.15	4.90	5.10	5.15	5.30	5.35
1:2.0	4.65	4.45	4.75	4.70	4.95	4.95
1:2.5	4.30	4.10	4.40	4.25	4.45	4.50
1:3.0	4.05	3.95	4.05	4.10	4.25	4.30
1:3.5	3.95	3.95	4.00	4.05	4.15	4.15
1:4.0	3.70	3.65	3.85	3.85	4.20	4.25
1:4.5	3.65	3.60	3.65	3.60	4.05	4.10
1:5.0	3.55	3.50	3.60	3.55	3.80	3.85

DISCUSSION

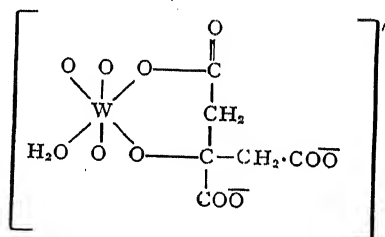
The results of conductivity and pH of the system Na_2WO_4 -tartaric acid (Tables I and II, Fig. 1) show that a complex of tartrate-tungstate is formed in equimolecular proportions. There is a sharp rise in conductivity and fall in pH till the ratio 1:1 is reached after which the rise in conductivity and fall in pH are slow and gradual showing thereby that a complex which has greater electrical conductivity and lower pH value than its components is formed. The high electrical conductivity shown by tartaric acid-tungstate complex is due to the presence of tartaric acid which may cause the dissolution of the colloidal particles or micelle ions, to give ions of greater electrical conductivity as pointed out by Biswas² in the case of tartaratomolybdates. On ageing, the system showed lower conductivity and higher pH values in comparison with those of the fresh system, at all ratios, indicating thereby that the complex formed undergoes decomposition into its constituents. Therefore, the complex formed between sodium tungstate and tartaric acid is additive and does not involve the elimination of the water molecule. The formation of the complex is shown by the following reaction:



and its constitution may be represented as below with a molecule of water as one of the co-ordinating groups.



In the case of citric acid-tungstate complex also, the results of conductivity and pH measurements show an inflection at equimolecular proportions of sodium tungstate and citric acid (Table III and Fig. 2). The conductivity curves are similar to those of oxalato-tungstates rather than of tartaric acid and tungstate complexes. The nature of the curves and the inflection do not show an enhanced conductivity or low pH at the stage of the formation of the complex (unlike in the case of tartaric acid complex). On *par* with the tartarato- and oxalato-tungstate complexes, the citrato-tungstate complex should be represented as $(\text{WO}_3 \cdot \text{C}_6\text{H}_6\text{O}_7 \cdot \text{H}_2\text{O})$ with a molecule of water occupying one of the co-ordinate positions. The constitution of the citrato-tungstate complex may be represented as



The effect of ageing in this system also is similar to that in the case of tartaric and oxalic acids. The complex undergoes decomposition on ageing which is shown by the increase in conductivity and fall in pH of the system. The results of ageing support the view that the water molecule is one of the six co-ordinate groups of the complex and that the reaction is totally additive as in the case of tartaric and oxalic acids.

I express my grateful thanks to Dr. S. N. Banerjee and to Dr. A. K. Bhattacharya for their kind interest in this work.

REFERENCES

1. RAO AND BANERJI, 1954, *Proc. Nat. Acad. Sci., India*, **23**, 76.
2. BISWAS, A. B. 1947, *J. Ind. Chem. Soc.*, **9**, 345.

ANALYSIS AND COMPOSITION OF THE PRODUCTS OBTAINED IN THE SYSTEMS OF TUNGSTATES WITH MINERAL ACIDS ON AGEING *

BY G. S. RAO AND S. N. BANERJEE

(Department of Chemistry, University of Saugar, Saugar)

THE changes in electrical conductivity and pH of the systems of tungstates with mineral acids have been discussed in previous communications to this Journal.^{1, 2} Apart from these changes, it was mentioned that certain precipitates were obtained on ageing at different tungstate/acid ratios in each system. Just after 48 hours of ageing, the solutions containing acid ratios higher than 1:2 in the case of HCl, 1:3 in the case of HNO₃ and 1:4 in the case of H₂SO₄, developed turbidity and the precipitation was complete within 2 weeks. The precipitates were white and flocculent at first and then turned gradually yellow and settled down to a small mass.

These yellow products, which were finally obtained in various systems of ageing, were analysed on the same lines as in the case of the molybdate systems. The products were analysed for the following:

- (1) water of crystallization;
- (2) water-soluble and water-insoluble portions; and
- (3) content of WO₃ and sodium if any in the water-soluble and water-insoluble portions.

(1) *Water of crystallisation.*—The substance of a known weight was heated at a temperature between 150° to 200° C. and the loss of weight, if any, on heating determines the amount of water of crystallization. However, the products were found not to contain any water of crystallisation.

(2) *Water-soluble and water-insoluble portions.*—The water-soluble and water-insoluble portions are determined in the following way: about 0.5 gm. of the product was treated with 50 c.c. of distilled water and heated on a water-bath with constant stirring. The solution was allowed to settle and filtered through a weighed dry gooch crucible. The insoluble portion was left in the crucible. The gooch was dried and weighed again with the insoluble part. The difference in weight of the crucible with and without the insoluble portion gave the weight of the insoluble one. The difference in the

* Read at the Annual Meeting on 28th December 1954.

weight of the original product taken and the weight of the insoluble portion gave the weight of the water-soluble portion which was found to be negligible in every case.

(3) *Estimation of WO_3 .*—The substance which was insoluble in water was dissolved in excess of ammonium hydroxide. The solution was evaporated and an excess of concentrated HNO_3 and HCl were added. The yellow precipitate of tungstic acid or $WO_3 \cdot H_2O$ obtained was digested for about 30 minutes. To this digested mass, 20 c.c. of hot 5% solution of ammonium nitrate was added; the mixture was allowed to stand for some time and then filtered. The precipitate was washed first with ammonium nitrate solution, acidified with a few drops of HNO_3 , and finally with distilled water. The precipitate was then dried and transferred to a watch-glass. The filter-paper was ignited separately (to avoid reduction of WO_3) in a weighed porcelain crucible and then the precipitate on the watch glass was also transferred into the crucible. The contents of the crucible were heated strongly, cooled and weighed as WO_3 .

(4) *Estimation of the Sodium.*—The filtrate after the removal of tungsten was evaporated and heated strongly to remove all the ammonia. The residue was dissolved in water and tested for sodium by zinc through acetate. No precipitate was obtained showing, thereby, the absence of sodium.

In the following tables, the results of analysis of the products obtained on ageing the systems of Na_2WO_4 with HCl , HNO_3 and H_2SO_4 are given:—

TABLE I

Ratio $Na_2WO_4 : HCl$	Weight of product gm.	Amount of WO_3 gm.	Percentage of WO_3
1:2.5	0.2561	0.2380	92.95
1:3.0	0.2464	0.2289	92.90
1:3.5	0.2345	0.2177	92.82
1:4.0	0.2485	0.2303	92.79
1:4.5	0.2365	0.2197	92.86
1:5.0	0.2415	0.2244	92.92

TABLE II

Ratio Na_2WO_4 : HNO_3	Weight of the product gm.	Amount of WO_3 gm.	Percentage of WO_3
1:3.5	0.2256	0.2094	92.85
1:4.0	0.2267	0.2103	92.92
1:4.5	0.2204	0.2046	92.90
1:5.0	0.2284	0.2121	92.88

TABLE III

Ratio Na_2WO_4 : H_2SO_4	Weight of the product gm.	Amount of WO_3 gm.	Percentage of WO_3
1:4.0	0.2465	0.2290	92.91
1:4.5	0.2312	0.2149	92.96
1:5.0	0.2367	0.2200	92.92

CONCLUSION

The results of the analysis of the yellow products obtained in various systems on ageing show that (1) all the products are insoluble in water; (2) they do not contain any water of crystallisation; (3) they do not contain any sodium; and (4) the percentage content of WO_3 in all the products is nearly the same; the average value is 92.89%.

The calculated percentage of WO_3 in H_2WO_4 (92.80) corresponds nearly to the percentage content of WO_3 (92.89) of the products analysed. Therefore, the yellow products obtained from all the systems on ageing are the same, *i.e.*, tungstic acid (H_2WO_4) and they do not contain any polytungstates.

We express our grateful thanks to Dr. A. K. Bhattacharya for his kind interest in this work.

REFERENCES

1. RAO AND BANERJEE, 1954, *Proc. Ind. Acad. Sci., India*, **23**, (2) 92.
2. RAO, *Ibid.*, 1954, **23**, (2) 99.

THE SYSTEMS OF SODIUM TUNGSTATE WITH MINERAL ACIDS—PART I *

BY G. S. RAO AND S. N. BANERJEE

(*Department of Chemistry, University of Saugar, Saugar*)

THE anionic condensation of molybdates and tungstates in acid solutions to form poly-salts has been the subject of study for many workers resulting in controversial results. Rosenheim and co-workers¹ were the first to try to give a constitution for poly-acids and poly-salts under the extension of Werner's theory for co-ordination compounds. However, their theory could not stand long as it was hypothetical in nature and had no experimental basis. The recent work on the aggregation of molybdates and tungstates to form poly-salts in presence of H^+ ions is due to Jander and his school.² Jander's work is mainly based in dialysis and self-diffusion measurements and it has thrown some light on the constitution and composition of poly-acids and poly-salts. Britzinger³ and Jander⁴ also studied the process of aggregation by electro-dialysis method and came to the same conclusions, as those by diffusion measurements. The experimental methods and assumption of Jander and Britzinger have been criticized by P. Souchay.⁵ From the conductometric result, Jander⁶ assumed that the aggregation of molybdates or tungstates would go on with the increase of H^+ ions in solution, till aggregates containing 6, 12 and even 24 atoms of molybdenum or tungsten are formed. This assumption of Jander was contradicted by many workers—Dumanski and co-workers,⁷ Britton and German⁸ and Bevan⁹—who held the general view that the aggregation of molybdates or tungstates proceeds in acid solution till a tetra molybdate or tungstate is formed which does not further aggregate or decompose even in strongly acid solutions.

Further, most of the work on poly-acids and poly-salts is confined to molybdates and much less work has been done with reference to tungstates. From our study of the systems of tungstates with mineral acids, we have found that ageing and the presence of certain salts have got significant effect on the systems. Further, we have observed that though the hydrogen-ions are responsible for bringing about the aggregation, the action of the mineral acid used for studying the systems is specific. These aspects of study have not so far received attention. In this paper we have studied the fresh and aged systems of sodium tungstate with HCl and HNO_3 .

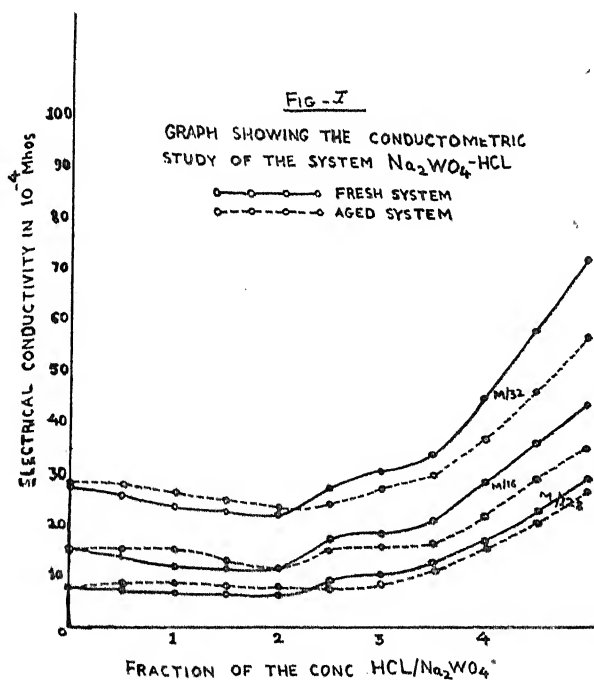
* Read at the Annual Meeting on 28th December 1954.

EXPERIMENTAL

For this study, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (A.R.), HCl (C.P.) and HNO_3 (C.P.) are used. The study of these systems is based on conductivity and pH measurements. Different sets of solutions were prepared to give tungstate/acid ratios ranging from 1:0 to 1:5 at concentrations M/32, M/64, M/128 of sodium tungstate. The conductivity and pH of the systems were measured when fresh and after intervals of 2, 4, 8 and 12 weeks in order to study the effect of ageing. The results, however, have been tabulated broadly under fresh and aged systems. Conductivity measurements have been made on the "New Doran" high precision conductivity bridge using a well platinised conductivity cell. The pH measurements have been made on Beckman standard pH apparatus using glass electrode. All the necessary precautions for conductivity and pH measurements have been taken.

DISCUSSION

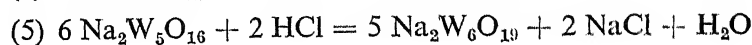
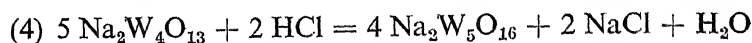
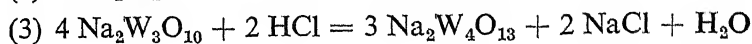
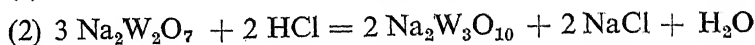
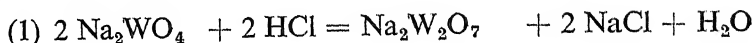
In the system $\text{Na}_2\text{WO}_4\text{-HCl}$ (Table I, Graph I) as the concentration of HCl increases, there is a gradual fall in the conductivity till the ratio, tungstate



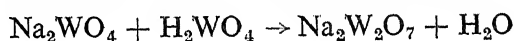
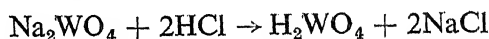
to HCl , reaches 1:2. Then there is a sudden rise in conductivity till the ratio about 1:2.5, after which the results are steady up to the ratio 1:3.5.

After this there is an abrupt rise in the conductivity results showing thereby that there is no further action of HCl on the system. In the system $\text{Na}_2\text{WO}_4\text{-HNO}_3$ the fall of conductivity is similar but it continues till the ratio 1:3, after which there is a sudden rise in conductivity till the ratio 1:3.5 is reached. Thereafter the results are steady till 1:4, beyond which the conductivity rises sharply showing that there is no further action of the acid on the system.

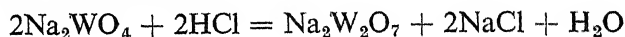
The above observations can be best explained if the process of aggregation is represented by the following equations which show that the aggregation takes place gradually and in a continuous manner:—



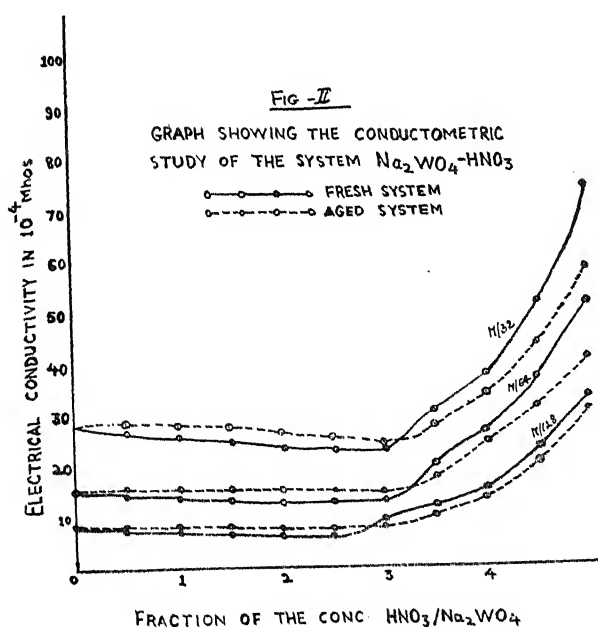
Again, the direct formation of the poly-tungstates in the above equations can be represented through an intermediate formation of tungstic acid before the polymerisation takes place. Thus the formation of tungstate can be represented by:



instead of by the equation,



The gradual and slight decrease in conductivity of the system, $\text{Na}_2\text{WO}_4\text{-HCl}$ up to the ratio 1:2 is due to the formation of successive poly-tungstates leading to the formation of the meta- or tetra-tungstate according to the equations 1, 2 and 3. The sharp rise in conductivity after the ratio 1:2 is due to the formation of the hydrogen salt of the tetratungstate, the formation of which goes on till the ratio 1:3.5 is reached. The steady conductivity results between the ratios 1:2.5 to 1:3.5 indicate the completion of the formation of the hydrogen salt of the tetra-tungstate. The sharp rise in conductivity again after the ratio 1:3.5 is due to the liberated tetra-tungstic acid along with the non-reacting HCl. The fall in conductivity of the system $\text{Na}_2\text{WO}_4\text{-HNO}_3$ (Table III, Fig. 2) till the ratio 1:3 is due to the formation of a hexa-tungstate which requires 2.9 molecules of acid per molecule of sodium tungstate. The sharp rise in conductivity after this ratio is due to the formation of the acid hexa-tungstate (similar to the acid



tetra-tungstate in the system $\text{Na}_2\text{WO}_4\text{-HCl}$). The steady conductivity between 1:3.5 to 1:4 is due to the completion of the formation of the acid tungstate. The sharp rise in conductivity again after the ratio 1:4 is due to the liberation of polytungstic acid along with non-reacting HNO_3 . The formation of a hexa-tungstic in this system is due to the liberation of a more reactive tungstic acid, possibly the tetrabasic acid, *i.e.*, para-tungstic acid H_4WO_5 or $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ which is responsible for bringing about the aggregation of tungstate ions till the formation of a hexa-tungstate in the system.

The factor of concentration of Na_2WO_4 .—The systems of tungstate have been studied at concentrations of M/32, M/64, and M/128 of sodium tungstate. At higher concentrations than M/32, an immediate precipitation of tungstic acid took place even at lower acid ratios and hence the systems could not be studied at higher concentrations. The aggregation of tungstates is quite pronounced at concentrations, M/32 and M/64. No sharp inflections are however obtained at the M/128 concentration.

The effect of ageing.—The comparative results of conductivity and pH of the fresh and aged systems (12 weeks) are given in the tables (Tables I to IV). Just after 48 hours, the solutions containing acid ratios higher than 1:2 in the case of HCl , 1:3 in the case of HNO_3 developed turbidity and the precipitation is complete within 2 weeks. There is a fall in conductivity and

TABLE I
Conductometric Study of the System $\text{Na}_2\text{WO}_4\text{-HCl}$
Temperature 25° C.

Ratio of Na_2WO_4 to HCl	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	27.75	14.85	14.90	7.55	7.60
1:0.5	25.50	27.50	13.55	14.95	7.50	7.75
1:1.0	23.50	26.45	11.65	14.80	6.75	8.15
1:1.5	22.50	24.50	13.10	12.60	6.50	7.55
1:2.0	21.55	23.05	11.50	11.55	6.45	7.45
1:2.5	26.10	24.10	17.10	15.10	9.10	7.35
1:3.0	29.50	27.10	18.15	15.50	10.15	8.55
1:3.5	33.50	29.50	20.50	16.15	12.55	11.10
1:4.0	44.50	36.50	28.10	21.55	16.50	15.15
1:4.5	57.55	46.05	35.50	28.50	22.45	20.05
1:5.0	71.45	56.50	43.15	34.50	28.10	26.10

TABLE II
Potentiometric Study of $\text{Na}_2\text{WO}_4\text{-HCl}$ System

Ratio of Na_2WO_4 to HCl	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.10	6.85	6.80
1:0.5	5.85	5.50	5.85	5.55	6.25	6.20
1:1.0	5.05	4.50	5.20	4.75	5.50	5.45
1:1.5	4.35	4.05	4.45	4.30	4.85	4.80
1:2.0	4.05	3.95	4.40	4.35	4.50	4.50
1:2.5	3.75	3.75	4.25	4.25	4.30	4.30
1:3.0	3.60	3.70	4.00	4.20	4.00	4.10
1:3.5	3.60	3.75	3.95	4.15	3.80	3.85
1:4.0	2.95	3.30	3.50	3.75	3.25	3.30
1:4.5	2.20	2.60	2.85	3.20	2.60	2.65
1:5.0	1.70	2.15	2.10	2.75	1.90	1.90

TABLE III
 Conductometric Study of $\text{Na}_2\text{WO}_4\text{-HNO}_3$
 Temperature 25° C.

Ratio of Na_2WO_4 to HNO_3	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	27.55	14.85	14.90	7.55	8.15
1:0.5	26.15	28.85	14.10	15.50	7.10	8.05
1:1.0	25.50	27.50	13.55	15.45	6.65	8.05
1:1.5	24.50	27.00	12.85	15.10	6.50	7.85
1:2.0	23.10	26.10	12.50	15.00	6.10	7.50
1:2.5	22.50	25.00	12.50	14.90	6.05	7.00
1:3.0	22.50	24.10	12.65	14.50	9.10	8.10
1:3.5	30.10	27.50	20.10	17.50	11.50	10.05
1:4.0	37.15	33.55	26.50	24.45	15.10	13.50
1:4.5	51.10	43.10	32.10	30.95	23.50	20.50
1:5.0	74.10	57.50	46.15	41.10	33.10	30.50

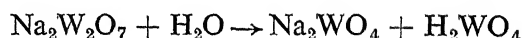
TABLE IV
 Potentiometric Study of $\text{Na}_2\text{WO}_4\text{-HNO}_3$ System

Ratio of Na_2WO_4 to HNO_3	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.05	6.85	6.90
1:0.5	6.25	5.90	6.35	6.15	6.45	6.40
1:1.0	5.40	5.15	5.85	5.05	5.90	5.85
1:1.5	4.40	4.30	4.90	4.80	5.25	5.25
1:2.0	4.15	3.55	4.20	4.05	4.70	4.65
1:2.5	3.65	3.40	3.90	3.75	4.15	4.05
1:3.0	3.55	3.40	3.65	3.85	3.95	4.10
1:3.5	3.45	3.75	3.80	3.90	3.80	3.85
1:4.0	3.15	3.30	3.55	3.80	3.35	3.40
1:4.5	2.40	2.80	3.05	3.45	2.70	2.75
1:5.0	1.55	2.20	2.35	3.20	1.90	1.95

rise in pH during the stage of precipitation in these solutions, after which, however, the conductivity and the pH remained constant. The precipitates which were obtained were first white and flocculent and changed gradually to yellow and settled down completely. The analysis and composition of these precipitates after the completion of the period of ageing is given in a separate communication. There is a gradual rise in conductivity and fall in pH on ageing solutions containing up to 1:2 in the case of HCl, 1:3 in the case of HNO_3 , due to the hydrolysis of polytungstates in these solutions. The change in conductivity and pH stopped after 8 weeks of ageing. For example, the mechanism of hydrolysis of di-tungstate is explained as below:—



or



The hydrolysis giving the products according to the second equation is more probable than the first one because the existence of a normal hydrogen tungstate is not known.

In both the systems the pH results are in accordance with those of the conductivity, and the same conclusions can be drawn from them also.

We express our thanks to Dr. A. K. Bhattacharya for providing us with the facilities to carry on this work.

REFERENCES

1. ROSENHEIM AND CO-WORKERS, 1921, *Abegg's Handbuch*, **4**, Part 1, ii, 977–1065.
2. JANDER AND SCHOOL, 1934, *Kolloid Beihefte*, **41** (1), 297; 1942, **54**, 1.
3. BRITZINGER, 1935, *Z. anorg. Chem.*, **224**, 97.
4. JANDER AND SAPNDAN, 1939, *Z. phys. Chem.*, **185**, 325; 1941, **188**, 65.
——— AND EXNER, 1942, *ibid.*, **190**, 195.
5. SOUCHAY, P., 1947, *Bull. Soc. Chem.*, France, **14**, 914.
6. JANDER AND CO-WORKERS, 1930, *Z. anorg. Chem.*, **194**, 413.
7. DUMANSKI AND CO-WORKERS, 1926, *Kolloid. Z.*, **38**, 208.
8. BRITTON AND GERMAN, 1930, *J. Chem. Soc.*, 2154.
9. BEVAN, 1943, *Chem. Soc. Ann. Reports*, 53.

THE SYSTEMS OF SODIUM TUNGSTATE WITH MINERAL ACIDS—PART II*

By G. S. RAO

(Department of Chemistry, University of Saugar, Saugar)

IN this paper, the systems of sodium tungstate with sulphuric and phosphoric acids have been studied. For this study, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (A.R.), H_2SO_4 (C.P.) and H_3PO_4 (C.P.) are used. The study of these systems also is based on conductivity and pH measurements. Different sets of solutions were prepared to give tungstate/acid ratios ranging from 1:0 to 1:5 at concentrations M/32, M/64 and M/128 of sodium tungstate. The conductivity and pH of the systems were measured when fresh, and after intervals of 2, 4, 8 and 12 weeks in order to study the effect of ageing. The results, however, have been tabulated broadly under fresh and aged systems. The experimental details for the measurements of conductivity and pH are the same as described in Part I of this communication.¹ The results of conductivity and pH of the fresh and aged systems of sodium tungstate with sulphuric and phosphoric acids are given in Tables I to IV and graphed in Figs. 1 and 2.

TABLE I

Conductometric Study of the System Na_2WO_4 —Tartaric Acid
Temperature 25° C.

Ratio of Na_2WO_4 to Tartaric acid	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.55	27.65	14.85	14.90	7.55	7.60
1:0.5	34.45	32.10	20.65	18.50	12.10	10.50
1:1.0	40.65	37.55	26.10	22.50	16.20	14.10
1:1.5	45.50	42.55	30.00	26.25	19.50	17.50
1:2.0	50.05	47.65	34.10	30.85	22.50	20.75
1:2.5	54.10	51.65	34.75	35.05	25.50	23.70
1:3.0	59.10	56.55	42.50	39.45	28.25	26.10
1:3.5	64.05	60.75	46.50	44.10	31.35	29.45
1:4.0	68.25	65.75	51.10	48.50	34.15	31.50
1:4.5	73.45	70.75	55.10	53.10	36.00	34.50
1:5.0	79.10	75.50	59.50	57.10	38.50	36.05

* Read at the Annual Meeting on 28th December 1954,

TABLE II

Potentiometric Study of the System Na_2WO_4 —Tartaric Acid

Ratio of Na_2WO_4 to Tartaric acid	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.25	7.15	6.85	6.90
1:0.5	5.10	5.30	5.45	5.65	5.90	5.95
1:1.0	4.55	4.65	4.80	4.95	5.40	5.45
1:1.5	4.45	4.65	4.75	4.85	5.15	5.20
1:2.0	4.05	4.35	4.60	4.70	4.65	4.70
1:2.5	3.80	4.10	4.10	4.40	4.40	4.45
1:3.0	3.50	3.65	3.85	4.25	4.15	4.20
1:3.5	3.15	3.35	3.55	3.75	3.90	3.95
1:4.0	2.95	3.15	3.30	3.50	3.60	3.65
1:4.5	2.75	2.95	3.20	3.30	3.45	3.50
1:5.0	2.60	2.10	3.10	3.25	3.35	3.40

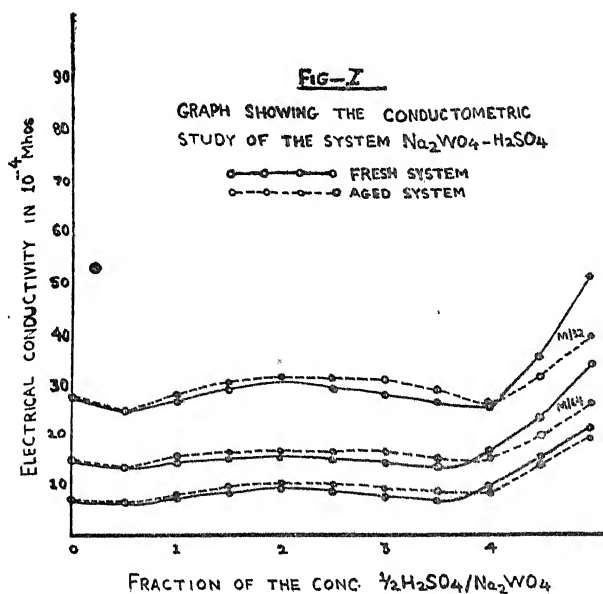
TABLE III

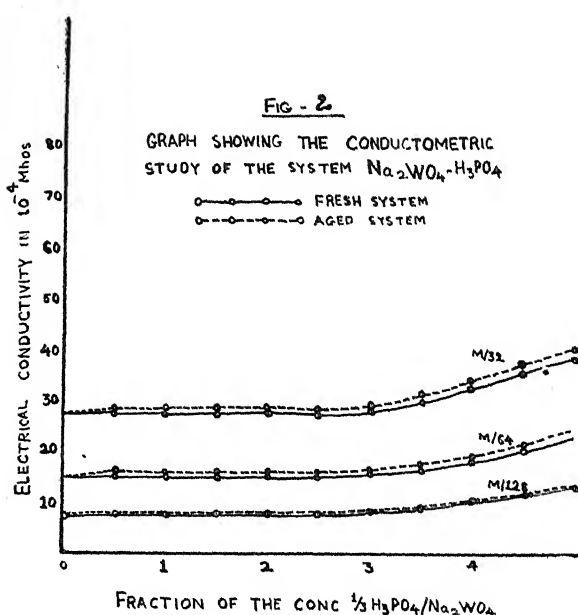
*Conductometric Study of Na_2WO_4 —Citric Acid**Temperature 25° C.*

Ratio of Na_2WO_4 to Citric acid	Conductivity in 10^{-4} mhos.					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	27.50	27.60	14.85	14.90	7.55	7.60
1:0.5	26.50	29.10	14.50	16.85	6.50	7.55
1:1.0	25.50	30.05	14.25	18.45	6.10	8.45
1:1.5	26.95	32.50	15.65	20.35	6.65	9.75
1:2.0	31.35	35.50	19.45	23.45	9.50	11.85
1:2.5	36.85	41.50	25.05	29.35	13.10	15.50
1:3.0	43.50	47.50	32.15	36.45	17.55	21.05
1:3.5	48.45	53.10	39.10	42.50	22.30	26.10
1:4.0	54.55	59.10	45.60	49.50	29.10	32.50
1:4.5	61.40	65.75	52.70	56.75	34.65	39.10
1:5.0	67.50	72.50	60.50	64.50	41.10	45.45

TABLE IV
Potentiometric Study of Na_2WO_4 —Citric Acid

Ratio of Na_2WO_4 to Citric acid	pH					
	Concn. of Na_2WO_4 M/32		Concn. of Na_2WO_4 M/64		Concn. of Na_2WO_4 M/128	
	Fresh system	Aged system	Fresh system	Aged system	Fresh system	Aged system
1:0	7.25	7.05	7.20	7.00	6.85	6.80
1:0.5	6.25	6.10	6.45	6.30	6.70	6.65
1:1.0	5.95	5.75	6.15	6.10	6.45	6.40
1:1.5	5.65	5.45	6.10	5.85	6.20	6.20
1:2.0	5.30	5.15	5.75	5.45	5.85	5.80
1:2.5	4.95	4.65	5.35	5.15	5.60	5.45
1:3.0	4.55	4.15	5.10	4.75	5.10	5.05
1:3.5	4.10	3.75	4.75	4.35	4.50	4.35
1:4.0	3.55	3.15	4.30	3.90	3.95	3.85
1:4.5	3.10	2.65	3.85	3.45	3.45	3.35
1:5.0	2.45	2.10	3.30	2.80	2.60	2.55





DISCUSSION

In the system $\text{Na}_2\text{WO}_4\text{-H}_2\text{SO}_4$, the conductivity falls upto the ratio 1:0.5 and there is turbidity in the solution. The conductivity then gradually increases till the ratio 1:2 after which again there is a fall in conductivity till the ratio 1:4 is reached. Thereafter the conductivity rises sharply indicating that there is no further action of the acid on the systems (Table I and Fig. 1). In the system $\text{Na}_2\text{WO}_4\text{-H}_3\text{PO}_4$, there is a slight fall in conductivity upto the ratio 1:3 after which there is a gradual and slight increase in conductivity (Table III, Fig. 2). The pH results (Tables II and IV) are in accordance with those of conductivity.

In the system $\text{Na}_2\text{WO}_4\text{-H}_2\text{SO}_4$, the slight turbidity and the fall of conductivity is due to the liberation of free and insoluble tungstic acid. The slight increase in conductivity after this ratio till 1:2 is due to the liberation of tungstic acid kept in solution without being reacted with Na_2WO_4 to bring about the aggregation. In this system, the anion of the acid has a definite influence on the liberated tungstic acid, prior to its reaction with a lower tungstate to form a higher poly-tungstate. Because of its slight positive charge as pointed out by Ehrlich and Moser¹ tungstic acid attracts sulphate

ions which have greater ionic radius and thus form a protective layer around the tungstic acid molecules retarding its reaction with a lower tungstate to form a higher poly-tungstate. However, with the increase of H^+ ions and after the ratio 1:2, the anionic effect is overcome and the aggregation takes place till the ratio 1:4 is reached, which is indicated by the fall of conductivity in that region. After the ratio 1:4, there is the usual rise in conductivity showing that there is no further action of the acid on the system. The aggregation in this case also should be upto the formation of a tetra-tungstate because the process of aggregation shown by the fall of conductivity is between two units of the acid (*i.e.*, between 1:2 to 1:4). However, there is no further inflection in this case, which shows that the acid tetra-tungstate is not formed. After the ratio 1:4, the sharp rise in conductivity is due to the presence of free non-reacting sulphuric acid. In $Na_2WO_4-H_3PO_4$, the results evidently show that phosphoric acid is not strong enough to bring about the formation of poly-tungstates. From the slight fall in conductivity and the minimum pH reached in the systems, the formation of a di- or tri-tungstate may be expected.

The factor of concentration of Na_2WO_4 .—These systems have been studied at concentrations of M/32, M/64 and M/128 of sodium tungstate. At higher concentrations than M/32 immediate precipitation of tungstic acid took place even at lower acid ratios and hence the systems could not be studied at higher concentrations. The results are quite pronounced at concentrations M/32 and M/64. No sharp inflections are obtained at the M/128 concentration.

The effect of ageing.—The comparative results of conductivity and pH of the fresh aged systems are given in Tables I to IV. Just after 48 hours in $Na_2WO_4-H_2SO_4$ system, solutions containing acid ratios higher than 1:4 developed turbidity and the precipitation is complete within 2 weeks. There was a fall in conductivity and rise in pH during the stage of precipitation in these solutions after which, however, the conductivity and pH remained constant. In this system also the precipitates which were obtained were first white and flocculent and changed gradually to yellow and settled down completely. The analysis of these precipitates after the completion of the period of ageing is given in a separate communication to this journal. There is a gradual rise in conductivity and fall in pH on ageing solutions containing upto 1:4 of H_2SO_4 due to the hydrolysis of poly-tungstates in these solutions. The change in conductivity and pH stopped after 8 weeks of ageing. The mechanism of hydrolysis of poly-tungstates formed in this system is the same as given in Part I of this communication. However,

there is practically no change on ageing in the systems with H_3PO_4 excepting a slight increase in conductivity at the initial acid concentrations.

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REFERENCES

1. RAO AND BANERJEE, 1954, *Proc. Nat. Acad. Sci., India*, **23**, 92.
2. EHRLICH AND MOSER, 1922, *Edel. Erden. Erze.*, **3**, 40, 65.

ULTRASONIC STUDIES ON THE COMPLEX FORMATION OF IODINE WITH SOLVENTS*

BY N. R. SUBBARATNAM AND A. K. BHATTACHARYA

(*Department of Chemistry, University of Sagar, Sagar*)

THE shattering power of high frequency sound waves has found its application in the dispersion of colloids and emulsification since a long time. Physical distortion of boundary surfaces is the cause of this. But the fact that these pulsating vibrations can also have such effect on molecular scale is a recently recognised one. Szalay¹ has succeeded in splitting up a number of highly complex molecules like starch, gum arabic, gelatin, sugar, para-formaldehyde and hexamethylene. Mark's study² on the viscosity changes in high polymers subjected to ultrasonic impact showed that these oscillations in liquid "undoubtedly contribute to the opening up of Van der Waal's bonds as well as the disruption of chemical bonds". Even in the case of dipole associations in associated liquids like ethyl alcohol, phenol, acetic acid and benzoic acid, depolymerisation was shown to be complete after prolonged irradiation to ultrasonics (Buonsanto³). The various chemical reactions promoted by ultrasonic agitation as studied by Wood and Loomis,⁴ Richard and Loomis⁵ and Beuthe⁶ were partly explained by a possibility that a chemical bond is ruptured and free radicals are produced. Though later studies indicated that the formation of H_2O_2 as an intermediate product in these oxidation reactions is a necessary prerequisite, strong favour seems to be there for the view about rupture. Recently Weissler, Cooper and Synder⁷ worked on the production of chlorine from CCl_4 saturated in water and their result was explained by Griffing⁸ as purely due to a rupture. The only requirement in all these cases is the presence of a dissolved gas, which is responsible for cavitation and subsequent transfer of energy from the ultrasonic waves. Active species are formed in the bubble in whose interface with the solvent a large energy is transferred from the ultrasonic vibrations (Elpiner and Kolasnikove⁹; Griffing⁸).

The object of this paper is to study the effect of such disrupting forces on the iodine-solvent complexes. Iodine with solvents of a donor type (Lewis' sense) forms a complex by a co-ordinate covalent link through a lone pair of electrons from O, S, or N atoms or the π electrons in the case of aromatic hydrocarbons. The views of Hildebrand and Benesi,¹⁰ Bowen¹¹

* Read at the Annual Meeting on 28th December 1954.

and Mulliken¹² are that these chemical combinations occur by means of polarised complexes of the type $R.I_2 \rightarrow R.I^+ - I^-$ the positive end of iodine being stabilised by the solvent. This was substantially proved in the case of pyridine by Zingaro *et al.*¹³ According to Bowen¹¹ these complexes are held by Van der Waals forces. It is our attempt here to see if there is any change in light absorption of these solutions when subjected to ultrasonic vibrations. It is the light absorption that characterises the nature of these iodine solutions (Kleinberg¹⁴).

EXPERIMENTAL

The ultrasonic generator was a piezo-electric one with an X-cut quartz as the transducer. The frequency was 3 megacycles/sec. The power of the radio frequency oscillator was 15 watts, and that of the quartz oscillator used here 1 watt per cm.² The transducer was mounted on one side of the reaction cell with a thin film of transformer oil for good acoustical contact, thin silver foils serving as terminals. The rectangular quartz cell with plane optically worked sides was mounted on a trough kept in the path of light from the source to the slit of a medium quartz spectrograph. The ultrasonic vibrations were allowed to pass in a direction perpendicular to the light path. Cu arc run by a 3 amp. D.C. current was the source of light. The method of taking the spectra was that of Dhar and Bhattacharya¹⁵ in their study on chemical reactivity.

The absorption spectra of the solution was first taken by striking the copper arc for 10". Then the transducer is set into oscillation and the photographs are taken at intervals upto 30 minutes. The changes in the intensity of the prominent copper doublets at 324.7 m μ and 327.4 m μ and the line 453 m μ were measured visually from the negatives by means of a magnifying micrometer eyepiece. The intensity changes could be roughly measured this way.

The thermal effect of ultrasonic waves are always to be taken into account. The total rise in temperature after 30 minutes agitation was never more than 8° C. on the average. So separate exposures were taken with solutions raised by 8° and none of them showed any considerable change in intensity. Therefore, the changes observed here were taken as the ultrasonic effect.

0.0005 M solutions of iodine in methyl alcohol, methyl acetate, dioxan, nitrobenzene and pyridine were thus studied. The intensity of the lines in the ultraviolet was decreasing with time in some cases and in some others there was no change. This decrease corresponds to a greater increase of absorption in the ultra-violet.

DISCUSSION

The greatest change was found in ethyl alcohol and there was absolutely no change in pyridine solutions. The others fall roughly in the following order:—

Ethyl alcohol > Acetone > Methyl acetate > Nitrobenzene
> Dioxan > Pyridine

This seems to indicate the differences in the stability of the solvent-solute complexes. It is of great interest to note that the study of Hartley and Skinner¹⁶ on the heat of complex formation also gives a measure of the stability. Though there is no direct means of measuring the absolute value of the heat of complex formation, these workers could calculate this in a relative way by measuring the deviation of these solutions from the behaviour of 'regular' solutions. The heats of complex formation (in k. cal./mole) so computed are:

Ethyl alcohol	..	2.1
Acetone	..	(Not given)
Methyl acetate	..	2.4
Nitrobenzene	..	2.75
Dioxan	..	3.25
Pyridine	..	7.95

The more positive the heat of complex formation the more stable will be the complex. So it appears that pyridine and dioxan should be among the stablest. Actually in the case of dioxan an extremely labile needle-shaped reddish compound of iodine and dioxan has been prepared by Kortum Seiler *et al.*¹⁷ The Pyridine compound was also considered to be highly stable by Hartley and Skinner.¹⁶ The results on light absorption in this paper has a very close agreement with this order of stability. The instability of the complex is found to result in an increase in light absorption in the ultra-violet when subjected to ultrasonic vibrations. In view of the fact that the complex is unstable and the forces that make it are fairly weak, the ultrasonic vibrations perhaps disturb the complex and liberate free iodine. The free iodine now can combine with I-radicals set free by ultrasonic agitation or with I⁻ existing in solution to form I₃⁻ ions. The maxima of I₃⁻ ion being at 290 mμ and 360 mμ, the greater production of it results in an increase in absorption in the ultra-violet. The stabler complexes do not exhibit

changes in the ultra-violet because the disruption of the complex and the production of I_3^- ions in such cases are less probable.

REFERENCES

1. SZALAY, 1933, *Z. Phys. Chem.*, **164**, 234.
2. MARK, 1945, *J. Acoust. Soc. Am.*, **16**, 183-87.
3. BUONSANTO, 1951, *Bull. Soc. Ital. Biol. Sper.*, **27**, 225-28.
4. WOOD AND LOOMIS, 1927, *Phil. Mag.*, **7** (4), 417.
5. RICHARD AND LOOMIS, 1927, *J. Am. Chem. Soc.*, **49**, 3086.
6. BEUTHE, 1933, *Z. Phys. Chem.*, **163**, 161.
7. WEISSLER, COOPER AND SYNDER, 1950, *J. Am. Chem. Soc.*, **72**, 1769-75.
8. GRIFFING, 1950, *J. Chem. Phys.*, **18**, 997-98.
9. EL'PINER AND KOLESNIKOVA, 1950, *Doklady Akad. Nank. S.S.S.R.*, **75**, 837-39.
10. HILDEBRAND AND BENESI, 1948, *J. Am. Chem. Soc.*, **70**, 3978; 1948, *ibid.*, **70**, 2832-33; 1949, *ibid.*, **71**, 2703.
11. BOWEN, 1950, *Quart. Reviews*, **3** (4), 243.
12. MULLIKEN, 1952, *J. Am. Chem. Soc.*, **74**, 811-24.
13. ZINGARO *et al.*, 1951, *ibid.*, **73**, 88.
14. KLENIBERG, 1948, *Chemical Reviews*, **70**, 3978.
15. BHATTACHARYA AND DHAR, 1934, *J. Ind. Chem. Soc.*, **11**, 311.
16. HARTLEY AND SKINNER, 1950, *Trans. Faraday. Soc.*, **332**, 621.
17. KORTUM SEILER *et al.*, 1950, *Z. electrochem.*, **54**, 70-73.